The influence of blowing agents type on foaming process and properties of rigid polyurethane foams*)

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Abstract: Rigid polyurethane foams (RPF) were synthesized with the use different type of blowing agents (methylal, isopentane, cyclopentane, mixture of isopentane and cyclopentane, carbon dioxide). The effects of blowing agent type on the foaming process, cellular structure, mechanical properties and changes of thermal conductivity during one year aging are described. As expected, the highest reactivity confirmed by the fastest decrease of the dielectric polarization and highest maximum of temperature was observed for polyurethane system blown with carbon dioxide. A small difference in the reactivity of systems foamed with physical blowing agents was also noticed – the most reactive was composition with cyclopentane. Cellular structure of foams blown by carbon dioxide was characterized by smaller cells size than foams where physical blowing agent were used. The lowest thermal conductivity after 360 days was observed for polyurethane systems foamed with isopentane and mixture of isopentane and cyclopentane. Regardless of the measurement time the highest thermal conductivity was characteristic for the materials blown with water and methylal. The foams with isopentane were characterized by the highest compressive strength.

Keywords: polyurethane, blowing agents, foaming process, reactivity, cellular structure, physical-mechanical properties.

Wpływ rodzaju poroforów na proces spieniania oraz właściwości sztywnych pianek poliuretanowych

Streszczenie: Sztywne pianki poliuretanowe (RPF) otrzymano z zastosowaniem różnych czynników spieniających (metylal, izopentan, cyklopentan, mieszanina izopentanu i cyklopentanu oraz ditlenek węgla). Analizowano wpływ rodzaju poroforów na proces spieniania, strukturę komórkową pianki, jej właściwości mechaniczne oraz zmiany właściwości termoizolacyjnych w ciągu jednego roku. Jak oczekiwano, największą reaktywnością charakteryzował się system spieniony za pomocą ditlenku węgla, czego potwierdzeniem są: najszybsze zmniejszenie polaryzacji dielektrycznej oraz najwyższa maksymalna temperatura w procesie spieniania. Niewielkie zmiany reaktywności zaobserwowano w wypadku systemów poliuretanowych spienianych z udziałem różnych czynników fizycznych – największą reaktywnością odznaczał się układ z cyklopentanem. Struktura komórkowa pianek otrzymanych z udziałem ditlenku węgla jako czynnika spieniającego charakteryzowała się komórkami o rozmiarach mniejszych niż rozmiary komórek w materiałach piankowych wytworzonych z zastosowaniem fizycznych czynników spieniających. Najmniejszy współczynnik przewodzenia ciepła po upływie 360 dni wykazywały pianki poliuretanowe spieniane za pomocą izopentanu oraz mieszaniny izopentanu i cyklopentanu. Niezależnie od czasu pomiaru największe wartości współczynnika przewodzenia ciepła zaobserwowano w wypadku materiałów piankowych otrzymanych z zastosowaniem wody i metylalu, natomiast największą wytrzymałość mechaniczną wykazywały pianki wytworzone z udziałem izopentanu.

Słowa kluczowe: poliuretany, czynniki spieniające, proces spieniania, reaktywność, struktura komórkowa, właściwości fizyczno-mechaniczne.

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Rigid polyurethane foams (RPF) can be applied as high efficiency thermal insulation materials in construction, pre-insulated pipelines and refrigeration industry due to their properties such as a closed-cell structure, low thermal conductivity and low moisture permeability [1]. In the literature, there are also described open-cell polyurethane (PUR) foams. However, the open-cell ones significantly increase the possibility to heat transfer and the foams with such structure are characterized by much more higher thermal conductivity than RPF with closed-cell structure [2].

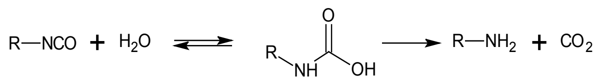
The basic aspect of the synthesis of foamed polyurethanes is the generation of foaming gas, which can be achieved by chemical reaction using chemical blowing agents, or physical phenomena of physical blowing agents evaporation [3]. Currently, the best thermal insulation properties of PUR foams are mainly determined by low thermal conductivity of blowing agents closed in foam cells.

In recent years environmental aspect influences on the development of blowing agents used in formulations of RPF. It is directly associated with their chemical structure. The use of halogenated compounds such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) is banned due to ozone layer depletion and global warming [4]. According to the Montreal Protocol nations should strive towards the total phase them out of production and application in polymeric materials [5].

Among the environmental criteria, the ozone depletion potential (*ODP*) and global warming potential (*GWP*) parameters are the most important. The *ODP* is an indicator that is a relative measure of the effect of a compound on the ozone layer. The chlorine radicals formed as a result of photochemical processes in the upper atmosphere break down the ozone molecules, causing the ozone layer to be destroyed. The percentage of chlorine in its molecule determines the effect of a given compound on the *ODP*. *GWP* is a relative measure of the potential impact on the climate caused by the presence of a chemical compound with the properties of a greenhouse gas in the atmosphere. *GWP* determines the level of infrared radiation absorption and durability of compounds in the atmosphere.

Currently, blowing agents used in chemical technology should have an *ODP* equal to 0 and the possibly lowest *GWP*. The PUR industry has increased interest in substances that do not contain chlorine atoms. Among considered blowing agents pentane isomers and fluorinated derivatives (HFCs) of ethane, propane and butane are mostly used. Significant disadvantage of HFCs is their cost which limits their common application [6].

More and more scientists are focused on developing RPFs based on water and mixture of chemical and physical blowing agent [5, 7–10]. Carbon dioxide is generated by the reaction between water and isocyanate, according to the Equation (1):


(1)

The subsequent reaction results in stiffening and strengthening polymer matrices due to urea bonds, and crosslinking biuret bonds that are part of rigid PUR segments [11]. However, the cost and availability of HFCs has led the RPF industry to focus on pentane and water as the primary blowing agent, especially in construction applications.

In this paper, the influence of blowing agents type on foaming process of PUR composition is described the first time. Moreover, cellular structure of foams prepared and their selected physical-mechanical properties are analyzed in correlation with foaming process parameters.

EXPERIMENTAL PART

Materials

The petrochemical polyol Rokopol RF-551 was supplied by PCC Rokita SA. The isocyanate Ongronat 2100 was supplied by BorsodChem. Polycat 5 produced by Air Products and Chemicals was used as a catalyst. A silicone surfactant with the trade name Niax Silicone L-6915 produced by Momentive Performance Materials Inc. was used as a stabilizer of the foam structure. The characteristics of blowing agents are shown in Table 1.

T a b l e 1. Characteristics of used blowing agents

Commercial product	Chemical name	Molar mass g/mol	Boiling temp. °C	Producer/ supplier	Symbol of PUR system
Water	Carbon dioxide	44.0	–	–	PU-CO2
NOVEXPANS™ cyclopentane/ isopentane (70/30)	Cyclopentane (70 %)/ 2-methylbutane (30 %)	70.7	38	Inventec Performance Chemicals	PU-NOV
Cyclopentane	Cyclopentane	70.1	48	Brenntag Polska Sp. z o.o.	PU-CYC
ISOPENTANE Q1111	2-Methylbutane	72.2	28	Shell Chemicals	PU-ISO
Metylal (pure)	Dimethoxymethane	76.1	42	Brenntag Polska Sp. z o.o.	PU-MET

T a b l e 2. The characteristic parameters of the PUR foaming processes

Parameter	PU-CO2	PU-ISO	PU-NOV	PU-CYC	PU-MET
Max rise height, mm/s	20.8	10.9	12.4	15.8	19.0
Max rise height occurrence time, s	21	33	34	39	33
Max temperature, °C	178	144	149	147	154
Max pressure, Pa	7676	5699	12 341	15 012	19 067
Max pressure occurrence time, s	57	118	129	135	112

Preparation of foam samples

Rigid PUR foams with different blowing agents were prepared using a one step method. The polyol – 100 parts, catalyst – 1.5 php (per hundred polyol), surfactant – 1.5 php, water – 1.5 php, and physical blowing agent – 12 php were mechanically stirred for 15 s to ensure their complete homogenization. After that the isocyanate was added to the polyol premix to obtain the ratio NCO/OH = 1.1/1.0. Next, the whole system was mechanically stirred for 7 s and poured into a mold. The symbols of PUR systems are shown in Table 1.

Methods of testing

– The foaming process was analyzed using the Foamat equipment. This analysis allowed determination such parameters during foaming process as: temperature, pressure and dielectric polarization. A detailed methodology was described in our previous paper [12].

– The morphology of cells was analyzed using a scanning electron microscope (SEM) Hitachi S-4700. The cell structure was also analyzed with using optical microscope. The analysis of cellular structure was performed in three cross-sections according to methodology presented in our previous paper [13]. The measurement of the content of closed cells was performed according to ISO 4590:2016.

– The thermal conductivity was determined using a Laser CompHeat Flow Instrument Fox 200. The measurements of thermal conductivity were made at an average temperature of 10 °C (temperature of cold plate 0 °C and warm plate 20 °C).

– The apparent density was measured according to ISO 845:2006.

– The mechanical properties of the foams were estimated in two directions, parallel and perpendicular to the foam rise direction according to ISO 844:2014 using Zwick Z005 TH Allround-Line.

RESULTS AND DISCUSSION

Blowing agent type *vs.* foaming process

The foaming process is one of the most important stages during the synthesis of porous PUR materials. At this stage, cells are nucleated and porous structure is

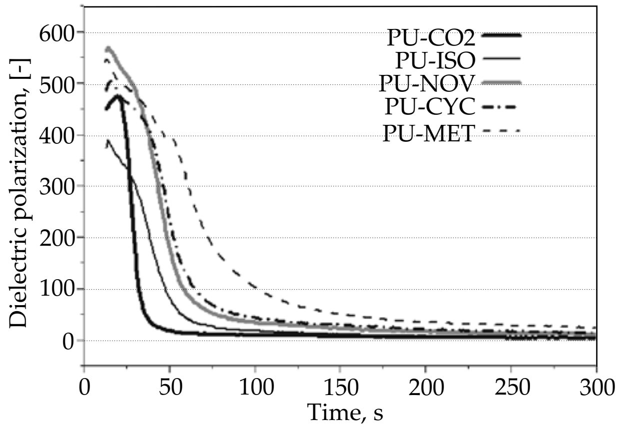


Fig. 1. The influence of blowing agent type on the dielectric polarization of reaction mixture during the foaming process

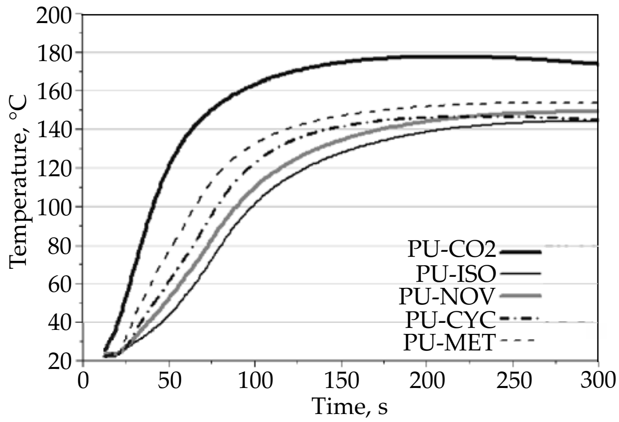


Fig. 2. The influence of different type of blowing agents on the temperature of reaction mixture during the foaming process

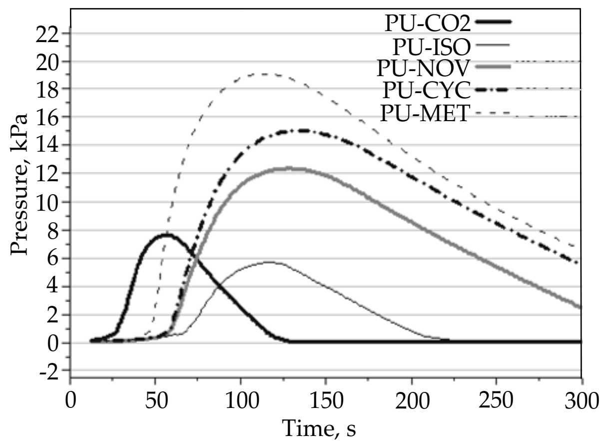


Fig. 3. The influence of different type of blowing agents on the pressure of reaction mixture during the foaming process

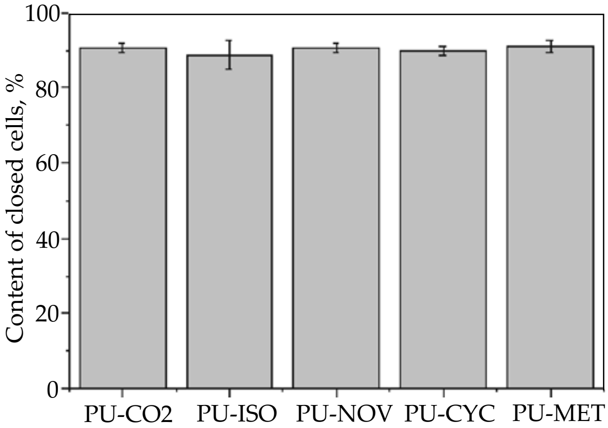


Fig. 4. Content of closed cells of obtained RPFs

created, which have a significant impact on the physical-mechanical properties of PUR foams including specially thermal conductivity. The second important aspect is gas closed in PUR foam cells. The composition of gases closed in the foam cells has considerable influence on thermal conductivity of final porous product.

The effect of selected commercially available physical blowing agents on the foaming process was analyzed using the Foamat device. As the reference sample PUR foam was obtained, using water as a chemical blowing agent, generating carbon dioxide in the reaction (1) with isocyanate. The characteristic parameters of the PUR foaming processes are shown in Figs. 1–3 and in Table 2.

Materials obtained without the addition of physical blowing agents (using only water as a chemical blowing agent) were characterized by the highest maximum temperature during the foaming process, which is related to the fact that the reaction of isocyanate with water is strongly exothermic [14]. On the other hand, PUR systems in which low boiling liquids were used as the physical foaming agents are characterized by maximal temperatures lower by approx. 30 °C comparing to reference PUR system. It was a result of the fact that a part of the heat of the occurring chemical reactions was used to evaporate the physical blowing agent and this process is endothermic [14].

Changes of dielectric polarization showed that the most reactive was reference PUR system foamed with carbon dioxide. Such effect is associated with the highest temperature during foaming process. The maximal temperature of this reaction mixture was *ca.* 16 % higher than mean temperature of systems foamed with the physical blowing agents.

The greatest pressure changes were observed for systems in which the blowing agent was methylal, which is directly related to the lowest reactivity of this PUR system (Fig. 1) and relatively high temperature (Fig. 2) of the reaction mixtures containing physical blowing agents.

Blowing agent type *vs.* cell morphology

Rigid PUR foams are mainly used as thermal insulation materials. An important factor determining the favorable thermal insulation properties of such materials is the high content of closed cells (Fig. 4) and the type of gas composition that is entrapped inside.

It was concluded that type of tested blowing agent had not significant influence on the closed cell content. This property in the case of all the foams was on similar level – *ca.* 90 %. However, a variation of cell size and anisotropy was noticed (Figs. 5–8).

These parameters can also affect the mechanical and heat insulating properties.

Size and shape of cells determine the mechanical properties by spreading the compressive stresses to the more numerous structures present in small cell size foams and more isotropic cells to avoid concentrating the stresses onto fewer larger cell structures. The smaller size of cells in PUR structure, the highest value of compressive strength as well as lower thermal conductivity. Taking into account heat transfer theory, about 10–15 % of the heat transfer of RPF can be directly attributed to the radiation, which can be minimized by reducing the cell size of the foam [15, 16].

In the literature, cell size of rigid PUR foams obtained by chemical foaming is known to be smaller than that obtained by physical foaming such as cyclopentane [17]. Han *et al*. synthesized foams with mixture of cyclopentane/distilled water (10.0/1.0, php) and distilled water only with four different silicone surfactants having different silicone/polyether ratios [18]. Taking into account one exemplary surfactant with content of 1.5 php (the same content as in the case of foams described in this paper) the cell size of foams blown by mixture of cyclopentane/distilled water and water only were *ca.* 450 and 290 μm,

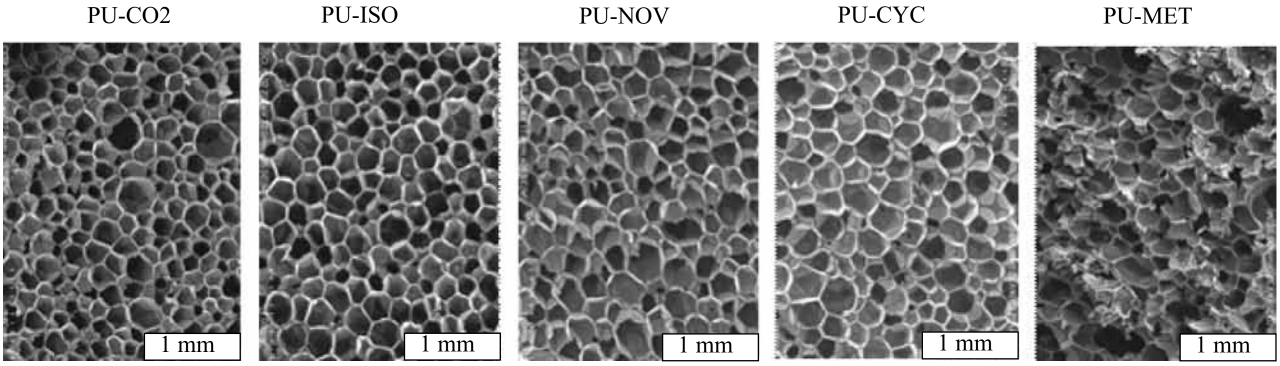


Fig. 5. SEM microphotographs of obtained RPFs

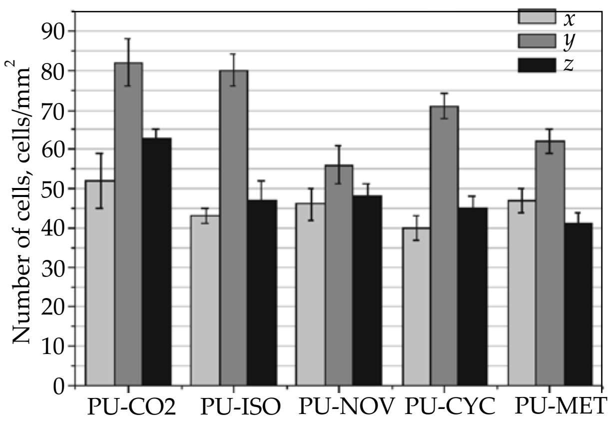


Fig. 6. Number of cells per cross-section area; system of determination of cross-sections in the horizontal mold: *x* – parallel to the foam rise viewed from the side, *y* – perpendicular to the foam rise, *z* – parallel to the foam rise viewed from the top

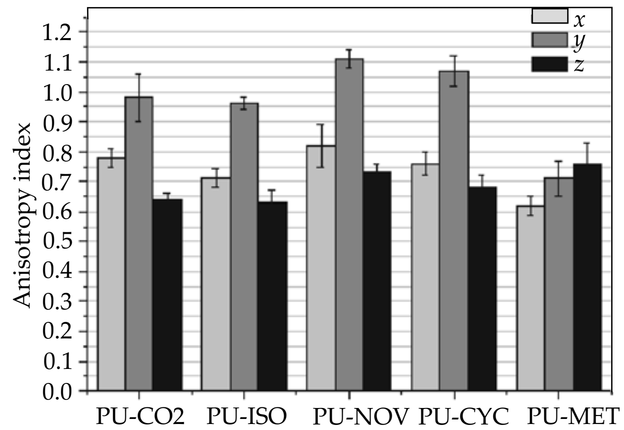


Fig. 7. Anisotropy index of cells

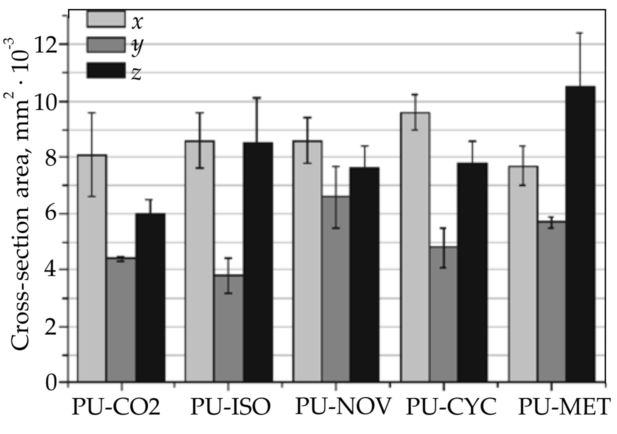


Fig. 8. Cross-section area of cells

respectively. Similar effect of smaller cells size of foam blown by water were also observed in our work. Choe *et al*. noticed different effect. In this case rigid PUR foams blown by physical blowing agent had smaller cell size than foam samples blown by chemical blowing agent [14]. Expansion of a foam is achieved by evaporation of low boiling agents or gas generation and in the case of physical blowing agents cellular structure is strongly dependent on temperature of reaction. The tendency to smaller

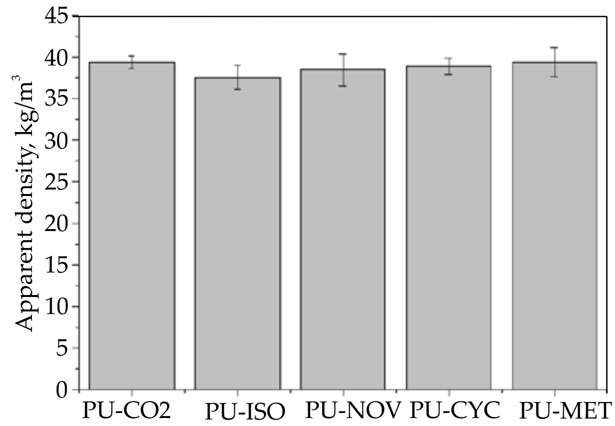


Fig. 9. Apparent density of RPFs foamed with different blowing agents

cells formation can be associated with higher reactivity of the PUR system foamed with water. Significant influence of PUR system reactivity is also confirmed by the analysis of cellular structure of foam prepared with different amount of gelling catalysts. Cell size of PUR samples decreased from 307 to 132 μm with increase of gelling catalysts content from 0.6 php to 1.8 php. In the case of blowing catalyst similar tendency was observed [14].

Blowing agent type *vs*. apparent density

Apparent density in the case of porous materials is a most important property to control mechanical and heat insulating properties. The values of apparent density for all foams obtained are shown in Fig. 9.

The apparent densities of the foams, nevertheless with different types of blowing agent, are similar and in the range 36–38 kg/m^3 what allow comparing mechanical and thermal properties of final RPFs.

Blowing agent type *vs*. thermal conductivity

Figure 10 shows values thermal conductivity of the tested foams *vs.* time. Initial measurements were carried out after 24 h, while the final effects of aging at room temperature were evaluated after *ca*. 1 year.

The lowest values of thermal conductivity were noticed for the materials foamed with cyclopentane. The biggest changes of thermal conductivity *vs*. time were observed for materials in which carbon dioxide (chemical blowing agent) and methylal (physical blowing agent) were used for foaming PUR systems. This effect may be related to the small particle size of these compounds, which facilitates their diffusion through the cell walls of the foam, as a result of which the air with a much higher heat conduction coefficient diffuses into the cells.

Blowing agent type *vs*. compression strength

The compression strength of PUR foams is determined as a force required for 10 % deformation of original di-

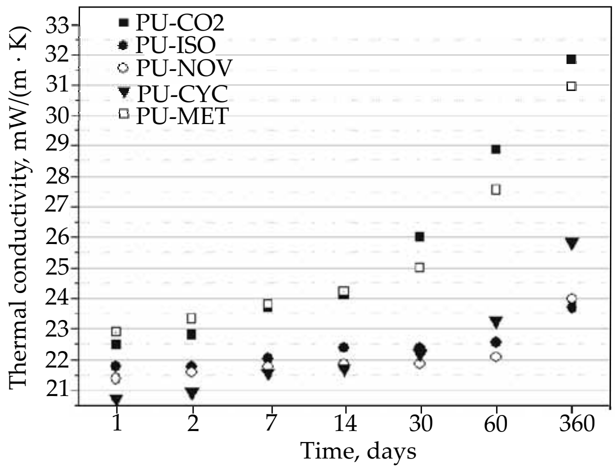


Fig. 10. Thermal conductivity *vs*. aging time of foams

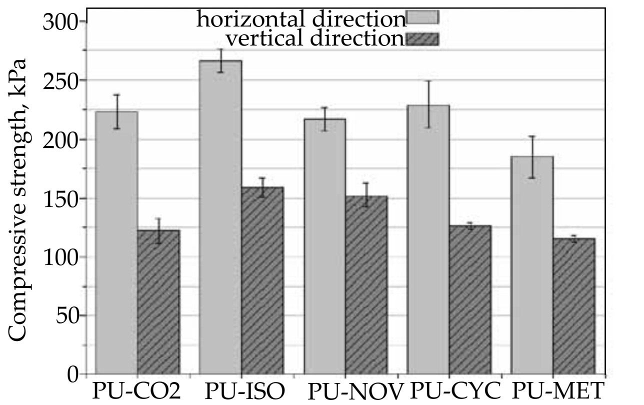


Fig. 11. Compressive strength of RPFs with different blowing agents measured in two directions

mension of the tested samples and it is closely related to its dimensional stability. Minimum compression strength to ensure dimensional stability for foams must be greater than *ca*. 0.1 MPa [19]. Figure 11 shows that all foams, which were obtained using different physical blowing agents have the values of compressive strength in both tested directions higher than 100 kPa.

Regarding the effect of blowing agent type, isopentane gives the highest compressive strength of foams, especially in the horizontal direction according to the foaming rise direction. It was also noticed that PU-MET foams were characterized by the lowest values of compressive strength measured in both directions. This is probably an effect of polyurethane matrix plasticization, that was the highest by methylal.

Li *et al*. have analyzed the influence of the water content (3 to 7 php) in polyol premix on the apparent density and compressive strength of final rigid foams [16]. They noticed, that the changes of compressive strength exhibited the same trend as the apparent density. The compressive strength of samples increased from 147 kPa to 401 kPa with the decrease of water level from 7 php to 3 php and as a consequence the increase of apparent density of foams from 27 to 45 kg/m^3.

CONCLUSIONS

In order to understand the effect of physical and chemical blowing agents on the foaming process of PUR system, as well as cellular structure, changes of thermal conductivity and mechanical properties of five series of the PUR foams with different physical and chemical blowing agents were investigated.

Regarding the foaming process, the PUR system foamed with chemical blowing agent gave shorter maximum rise height and pressure occurrence times, as well as the temperature of reaction mixture during foaming was the highest for this system.

Taking into account PUR systems foamed with physical blowing agents, there was not direct correlation between the changes of dielectric polarization and temperature of reaction mixture. The fastest decrease of dielectric polarization was observed for formulation with isopentane, while the measured temperatures were the lowest what can be associated with delaying of reactions due to evaporation of this blowing agent having the lowest boiling temperature. On the other side, a slower foaming process advantages a better cell structure, giving the foams with the lowest thermal conductivity after 1 year as well as the most favorable compressive strength.

The least satisfactory results were noticed for materials foamed with methylal. Rigid polyurethane foams with this physical blowing agent were characterized by not uniform cellular structure, a high value of thermal conductivity as well as the lowest compressive strength.

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P. Czyżewski, Ł. Skowroński, D. Sykutera, W. Rybarczyk, M. Chorobiński, M. Bieliński – Ocena efektów laserowego znakowania warstwy wierzchniej wyprasek z polipropylenu

G. Makomaski, J. Zieliński – Odpadowy poli(metakrylanu metylu) jako prekursor do otrzymywania węgli aktywnych (*j. ang.*)

J. Szulc, K. Lewandowski, K. Skórczewska, J. Sadkiewicz – Uwalnianie tymolu z plastyfikowanego poli(chlorku winylu) (*j. ang.*)